THE MODE OF ACTION OF DIFLUFENICAN AND POSSIBILITIES FOR IMPROVEMENT OF POST-EMERGENCE ACTIVITY

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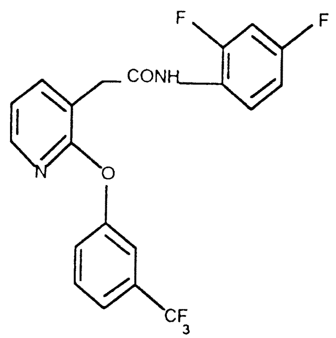
Summary. Diflufenican is a potent inhibitor of carotenoid biosynthesis active pre- and post-emergence. In post-emergence use the active is retained by the leaves but no useful phloem transport occurs. Trials showed that surfactants effective in reducing surface tension and increasing diflufenican solubility in the spray solution improved efficacy. Tankmixes of the diflufenican suspension concentrate plus MCPA emulsifiable concentrate were less efficacious than the co-formulated components. Beneficial effects of the solvents in the formulation are suggested to act as foliar penetration agents.

INTRODUCTION

Diflufenican (DFF) [N-(2,4-difluorophenyl)-2-(3-trifluoro-methylphenoxy)-3-pyridine carboxamide] is a member of the phenoxy nicotinanilide family (PNA) discovered in 1979 by Rhône-Poulenc Secteur Agro. The family is characterised by 3 essential rings:

- nicotine ring
- phenoxy ring attached at position 2
- carboxy anilinophenyl attached at position 3.



DFF has activity both as a pre-emergence and an early post-emergence herbicide. Its main activity is against broadleaf weeds but it also has interesting activity against certain important grass weeds. Susceptible species typically show symptoms of chlorosis and bleaching indicating that the major mode of action is on photosynthetic pigments.

Chlorophyll content is not affected directly by DFF since susceptible plants grown in dim light after treatment with DFF can accumulate more chlorophyll than similar plants grown in bright light (1).

The initial effect of DFF in affected tissues has been shown to be as a potent inhibitor of carotenoid biosynthesis causing accumulation of the carotenoid precursor phytoene. This indicates that the target site for DFF is the enzyme phytoene dehydrogenase, the target site of other bleaching herbicides such as norflurazn (2). DFF has no activity on pre-existing carotenoids and is most effective in growing tissues with rapid rates of carotenoid biosynthesis.

A major function of carotenoids is to protect chlorophyll and chloroplast membranes from photo-oxidation in bright light. The absence of carotenoids allows the photo-destruction of chlorophyll and causes the plant tissue to appear white, due to the absence of both carotenoid and chlorophyll pigments, showing the 'bleached' symptoms typical of DFF activity. A red pigmentation is often observed in DFF treated plants, especially grasses, due to stress induced anthocyanin production (3).

Pre-emergence activity. DFF is relatively immobile in soil due to adsorption and its low water solubility (log Kow = 4.9, water solubility = 0.01 µg/mL) and the majority is held in the top 1-2 cm of soil. The persistence of DFF in soil, combined with its low mobility is sufficient to provide weed control of species with protracted germination. To be effective, DFF must be absorbed by germinating weeds and translocated to the meristematic school tissues.

Seedlings originating below the DFF zone absorb DFF only through their shoots. Those originating in the DFF zone absorb DFF through their shoots and roots. Experiments have shown that shoot uptake is the major route of adsorption and uptake has been found to be greater for more susceptible species. Root uptake, although a less important route, is also greater in more susceptible species. Weed seedlings may be bleached on emergence and die rapidly. Seedlings of larger seeded species may have pigmented cotyledons but leaves subsequently develop symptoms. Cereal seeds germinate from below the DFF zone with the coleoptile protecting the young leaf as the shoot emerges. Any DFF absorbed moves towards the leaf tip rather than the meristem.

Post-emergence activity. Most material from a post-emergence application intercepted by plants will be retained by the leaves. DFF shows no useful phloem mobility, although some movement can occur, and DFF retained on or close to meristematic areas will therefore be important for post-emergence activity. Post-emergence applications of DFF hold interesting possibilities because only very low concentrations of DFF in meristematic areas are apparently necessary for activity. Formulation of herbicides can affect the activity of post-emergence applications by possibly affecting the retention of herbicide, its coverage of the plants and its penetration into the plants. Some aspects of DFF formulation have therefore been examined to determine opportunities for optimising biological activity.

MATERIALS AND METHODS

DFF was used as a suspension concentrate (S.C.) formulation, coded FR1078/3, containing 500 g/L DFF and as an emulsifiable concentrate (EC) coded FR1428/1, containing 150 g/L DFF. Both formulations were equivalent to commercially available formulations.

Laboratory trials were on plants grown in pots of John Innes No. 2 compost in glasshouses maintained at 25°C day and 15°C night temperatures with supplementary illumination for 14 hours per day. Spray applications were made to plants at the 2-3 leaf stage using a laboratory sprayer fitted with a SS8003E jet and applying a spray volume of 260 L/ha.

The ethoxylated alcohol surfactants Ethylan CD 103, 107 and 109, containing 2.9, 6.5 and 9.0 moles of ethylene oxide respectively, were obtained from Harcros Chemical Group.

The spread of 0.4 uL drops of solution applied by micrometer syringe to 'Parafilm' was determined by adding a water soluble dye to the solutions and measuring the areas of the dried deposits by image analysis.

The solubility of DFF in 1% solutions of surfactants was determined by HPLC analysis of filtered samples from the mixtures after equilibration.

RESULTS AND DISCUSSION

The effects of the addition of three alcohol ethoxylate surfactants with varied characteristics to sprays containing the S.C. formulation of DFF were examined. The three surfactants contained 2.9, 6.5 and 9.0 moles of ethylene oxide and all reduced the surface tension when added to water around 30 mN/M (Table 1).

All caused increased spreading of drops on a waxy surface with drops of solution containing surfactant CD 103 spreading the most. DFF solubility in 1% solutions of the surfactants was at least 90 times greater than in water, being highest in the solution of the surfactant CD 103.

Addition of all three surfactants to sprays of the S.C. formulation of DFF resulted in increased activity to levels similar to those obtained for acetone solutions of DFF (Table 1). Although addition of the surfactants increased the damage to barley it was not serious. Despite the differences in properties of the surfactants there were no differences in their effects on DFF activity. It may be supposed that the surfactants have varied effects on several processes including spray drop retention and spreading and penetration of DFF into shoot tissues, or, they may have similar effects on a major process such as DFF penetration. It has been reported that addition of surfactant to the S.C. formulation of DFF can considerably improve DFF penetration (4).

Table 1. Surfactant influence on DFF activity - Post-emergence

Surfactant	Mole ethylene oxide	Surface tension for 0.1% in water mN/m	Spread area for 0.1% in water mm^2	DFF solubility for 1% in water ug/mL	Activity for sprayed dose of 125 g/ha DFF as S.C. in water		
					Stellaria score¶	*Galium* % reduction green shoot tips	Barley % leaf area bleached
None	/	72	0.5	0.01	2.0	55	0.5
CD 103†	2.9	30	24	8.4	2.7	84	2
CD 107†	6.5	30	4	2.3	2.7	83	2
CD 109†	9.0	33	2	0.9	2.3	88	2
Acetone solution	/	/	/	100 mg/mL	3.0	75	10

† Ethylan CD : alcohol ethoxylate
¶ (5 = bleached + very stunted)
(0 = as control)

The S.C. formulation of DFF has been successfully developed and was used for the initial development of DFF in Australia. It has been commercialised for early post-emergence control of cruciferous weeds in lupins at does rates of 50-100 g/ha of DFF. Development of DFF for use in winter cereals in Australia evaluated mixtures of the S.C. formulation and MCPA or bromoxynil as ester E.C. formulations. Co-formulation of these components required that a non S.C. formulation of DFF be developed and an E.C. formulation was found to have good activity (Table 2). Co-formulation of DFF and MCPA ester in an E.C. formulation has been shown to improve activity relative to that of the tankmix (P. Buerger, pers. comm., 1987) possibly due to improved penetration. Use of this formulation type has allowed commercial levels of activity to be achieved with only 25 g/ha of DFF.

Table 2. Activity of DFF applied post-emergence
ED90 for weed species and ED10 for barley in g/ha

	Formulation		
	S.C. in water	E.C. in water	Acetone
Stellaria media	119	84	56
Galium aparine	1 055	117	368
Ipomoea purpurea	>500	64	82
Barley	>>500	≥500	250

REFERENCES

1. Wightman, P. and Haynes, C. 1985. Proc. Brit. Crop Prot. Conf. - Weeds. pp 171-178.
2. Barry, P. and Pallett, K. 1988. Proc. EWRS Symposium. pp 51-56.
3. Pallett, K. 1991. Premier Symposium DFF, Versailles. pp 67-72.
4. Knight, H. and Kirkwood, R. 1991. Pestic. Sci. 33, 305-317.